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(54) EFFICIENT METHOD OF PRODUCTION OF PECTIN FROM PLANT MATERIAL

SPECIFICATION

1. TITLE OF THE INVENTION

Efficient Method of Production of Pectin from Plant Material

2. CLAIMS

1. A method for producing a pectin comprising adding an aqueous solution of an acid and/or an inorganic salt into a plant pectin-containing material and heating the same so as to extracting the pectin, characterized by adding a quaternary ammonium salt and/or quaternary ammonium base belonging to cationic surfactants to the aqueous solution.

2. A method for producing a pectin as set forth in claim 1, setting the amount of addition of the quaternary ammonium salt and/or the quaternary ammonium base to 0.001 to 10 wt% of the plant pectin-containing material.

3. A method for producing a pectin as set forth in claim 1 or 2, setting a pH value of the aqueous solution for extracting the pectin to which the quaternary ammonium salt and/or quaternary ammonium base is added to 1 to 6.

3. DETAILED DESCRIPTION OF THE INVENTION

[Field of Utilization in Industry]

The present invention relates to an efficient method of production of a pectin from plant pectin-containing materials, in further detail, relates to a method of production for decomposition and extraction of the pectin from a plant material at which

time adding a quaternary ammonium salt and/or quaternary ammonium base so as to cause the plant tissue to swell, promote elution of the pectin into the extract, and remarkably improve the extraction rate.

Pectin is useful for filling the spaces among cells in a plant and thereby holds the plant tissue so plays an important role as a substance in the cell membrane. It is widely distributed in parts of plants such as the fruit, leaves, stem, root, rhizome, and tuber.

Further, pectin is added to food. It is attracting attention as a gelling agent when producing jelly, jam, marmalade, etc., a shape retention stabilizer of ice cream, sherbet, milk products, etc., a property stabilizer of soft drinks, a humectant of bread, an aging prevention agent, and a transparent edible coating agent of food and also a food for lowering the blood cholesterol and a low-calorie food medically as well.

As the conventional method of production of a pectin, generally the following method has been carried out. Namely, the following technique is usually used industrially: (i) finely crushing squeezed lees of fruit juice or other plant materials, heating the result to destroy the enzymes to prevent the decomposition of the pectin, then washing the result by water, then decomposing by an acid to render the pectin to a water soluble state, filtering this pectin extract using a filter aid, active carbon etc., filtering off the insoluble decomposed residue, purifying and neutralizing the result, then condensing it; (ii) then adding an alcohol to this purified condensed liquid to cause the pectin to precipitate and settle; and (iii) extracting this precipitate, washing it by water-containing alcohol, then by high purity alcohol and drying the result to obtain the pectin.

The inventors considered how to improve this general method of production and considered the various steps of the process. As a result, they took note of the extraction from the plant material in the step of the above (i). Namely, they investigated if the general method of production allowed the pectin to be sufficiently extracted from plant material such as the squeezed lees of fruit juice as expected. Since pectin is a polymeric substance having molecular weight of about 10,000 to 400,000, it is surmised that the decomposition and extraction of pectin from complex plant tissue is considerably difficult.

Therefore, they engaged in various studies on the addition of a quaternary ammonium salt or quaternary ammonium base for the purpose of facilitating permeation of the decomposed extract into the plant cell tissue and of causing swelling between cells of the plant tissue and of the cells themselves to help the dispersion and destruction thereof and facilitating extraction of the pectin contained in the plant as much as possible based on these two functions. As a result, they discovered that the extraction

rate of pectin was remarkably improved by the addition of small amounts of these and thereby reached the present invention.

Note that this quaternary ammonium salt or quaternary ammonium base has an enormous water solubility and is easily soluble also in alcohols, therefore it can be easily removed. Usage causes no concern in view of food safety.

As the plant pectin-containing material according to the present invention, use can be widely made of the fruit, leaves, stem, root, rhizome, and tuber of mandarin oranges, Chinese citron, oranges, grapefruits, lemons, shaddocks, etc. of the Rutaceae, strawberries, plums, pears, apples, peaches, apricots, etc. of the Rosaceae, grapes of the Vitaceae, pineapples of the Bromeliaceae, and sugar beets of the Chenopodiaceae, or squeezed lees of juice of the same. Particularly, irrespective of the fact the treatment of squeezed lees as waste material has been studied with greater effort at juice makers and sugar making factories, at present only part of it is being utilized as fertilizer and as bulking agents of feed for domestic animals etc. Most of it is being discarded in actual circumstances.

Accordingly, it is very important from the viewpoints of reuse of resources to make good use of lees as material of the relatively high added value pectin.

As apparent from the above description, the object of the present invention is to provide a novel method for producing pure, good pectin economically and efficiently.

Below, a detailed description will be given of the constitution and effects of the present invention.

Any part containing pectin of a plant can be used as the plant pectin-containing material used in the present invention, but woody parts classified as soft wood and hard wood requiring strong processing such as peeling, chipping, and digestion are not so suitable since the pectin is liable to decompose under these strong processing conditions. The fruit (including the peel, pulp etc.), leaves, stem, root, rhizome, and tuber of a plant as mentioned above containing a small amount of resin or lignin or their squeezed lees are preferred as materials, particularly squeezed lees are very suitable as the material for producing a pectin.

In general, when extracting a component of a plant material from the material, use is made of water, an organic solvent, or a mixed solvent of the same, an acid, an alkali, an oxidizing agent, etc. The proper decomposition and extraction conditions are always selected after considering the physical properties and chemical properties of the intended component, that is, the dissolvability, chemical resistance, decomposability, heat resistance, etc., but in the present invention, in order to promote the permeation of the decomposed liquid into the space among cells, dissociation among cells, and the

permeation of the decomposed liquid into the cells via the action of a surfactant such as a quaternary ammonium salt or base thereof between cells and on the cells per se in the plant tissue being extracted, swelling and destruction of the cells are induced up to the limit so as to thereby remarkably promote the extraction action by the decomposed liquid and thus efficiently and easily achieve the extraction of the pectin.

The quaternary ammonium salt or quaternary ammonium base referred to here belongs to the class of cationic surfactants among surfactants. As will be exemplified below, all of them can be applied to the present invention. Note that, a quaternary ammonium salt changes to a base by the addition of an alkali like:

$$\begin{bmatrix} & R' & \\ R & N & R''' \\ & R'' & \end{bmatrix} \bullet Cl \overset{NaOH}{\rightarrow} \begin{bmatrix} & R' & \\ R & N & R''' \\ & R'' & \end{bmatrix} \bullet OH$$

Therefore, the following examples are shown in the form of salts, but the same is also true also bases.

Alkyl(C^8 to C^{18})trimethyl ammonium bromides, alkyl(C^8 to C^{18}) trimethyl ammonium chlorides, alkyl(C^8 to C^{18})trimethyl ammonium iodides, alkyl(C^8 to C^{18})dimethyl ammonium bromides, alkyl(C^8 to C^{18})dimethyl ammonium chlorides, alkyl(C^8 to C^{18})dimethyl ammonium iodides, methyldiethyloleylamidoethyl ammonium chloride, trimethyldodecylthiomethyl ammonium chloride, methyldiethyloctylthioethyl ammonium chloride, methyldiethyloctylthioethyl ammonium iodide, trimethyldodecylmethylaminoethyl ammonium bromide, alkyl(C^8 to C^{18})dimethylbenzyl ammonium chlorides, trimethylbenzyl ammonium chloride, alkyl(C^8 to C^{18})pyridinium chlorides, alkyl(C^8 to C^{18})pyridinium bromides, 2-dodecylisoquinolinium bromide, alkyl(C^8 to C^{18})γ-picolinium bromides, and alkyl(C^8 to C^{18})-picolinium chlorides.

Further, the amount of addition of the quaternary ammonium salt or quaternary ammonium base is influenced by the decomposition and extraction conditions, that is the inorganic salts, acid, pH, extraction temperature, and extraction time and the type of the plant material, but desirably is 0.001 to 10 wt%, particularly 0.01 to 5 wt%, of the plant material. When the amount of addition is 10 wt% or more, the extract is conspicuously colored and the coloring of the obtained pectin is remarkable, so this is not preferred.

As the added inorganic salt, use is made of table salt, polymerized phosphates,

phosphates, an ammonium salt, etc. These are used for making the insoluble pectin soluble. As the acid, use is made of an organic acid or an inorganic acid. Usually use is made of mineral acids, for example, sulfuric acid or hydrochloric acid. As an organic acid, use is made of acetic acid, oxalic acid, etc.

The pH of the added aqueous solution of the quaternary ammonium salt and/or quaternary ammonium base when decomposing a plant material and extracting the pectin is preferably 1 to 6, further preferably 2 to 3. Further, the decomposition and extraction time is usually 30 minutes to 2 hours. The extraction temperature is room temperature to 100°C, preferably 40 to 90°C.

By the procedure under these conditions, the plant pectin-containing material becomes an amorphous solid. The pectin is eluted into the decomposition and extraction solution. Note that, needless to say, stirring and fine division of the material as much as possible are important in order to raise the extraction efficiency at the time of decomposition and extraction. Further, by adding a quaternary ammonium salt or quaternary ammonium base classified as a cationic surfactant, the permeation of the decomposition and extraction solution the inside and outside of the cells is promoted by the surface active action with respect to the pectin existing in the tissue of the plant material to be extracted and existing among cells and, at the same time, swelling of the cells is induced also for the cells per se and cell destruction is positively promoted, whereby a remarkably excellent decomposition and extraction effect in comparison with the case of the conventional decomposition and extraction is exhibited. This will be clearly recognized also from the following examples and comparative examples. Namely, the pectin content in the decomposition and extraction filtrate remarkably increases and also the amount of the extract per se increases, so the excellent effect of addition of the quaternary ammonium salt or quaternary ammonium base can be confirmed. Note that, also at the time of filtration, the secondary effects that the state of the extraction residue remarkably changes by the addition of the quaternary ammonium salt or base and the filtration becomes easy in comparison with the case of filtration in the case where a quaternary ammonium salt or base is not added and where the filtration is very difficult are found. Clearly this becomes great advantage in selecting a filtration machine and a filter agent at the time of industrialization. Further, in short, it goes without saying that the improvement of the extraction effect becomes a great plus from the viewpoint of the effective utilization of resources. Note that, as shown also in the examples, it is confirmed that the quaternary ammonium salt or base does not exist in the obtained pectin product, i.e., it can be easily and completely removed in the purification step.

Note that a quaternary ammonium base immediately changes to a quaternary ammonium salt by the action of the acid and/or inorganic salt coexisting in the decomposition and extraction solution, therefore there nothing stopping regarding the action and effect thereof as being completely the same as those of a quaternary ammonium salt.

Below, the invention will be explained by showing examples and comparative examples, but of course the technical scope of the present invention is not limited to them.

Example 1

1.5 liters of water was added to 500 g of washed squeezed lees of fruit juice of apples, 1 g (0.2 wt% with respect to the material) of benzyltrimethyl ammonium chloride (guaranteed reagent made by Nakarai Chemicals Ltd.) was added, and the mixture was heated and stirred. When the liquid temperature became 80°C, dilute sulfuric acid was added to adjust the pH to 3, then the result was heated and stirred at the same temperature for 1 hour for the decomposition and extraction. Next, this was filtered. The filtration was smoothly carried out in comparison with the comparative examples. Further, this filtrate was centrifugally separated under conditions of 11,000 rpm by using a centrifuge to remove the fine floating components and residue, then an aqueous solution of dilute sodium carbonate was added to adjust the pH to 6 and thereby obtain a purified filtrate. The yield of this purified filtrate was 1,400 g. Further, the pectin content in this filtrate was 4,850 γ/ml as a galacturonic acid. Note that, a quantitative method of this pectin was according to a report by both of MR. Ito and MR. Tada disclosed in a report of a fruit tree laboratory, series B, NO. 5 (1969), pp. 63 to 65. Incidentally, γ is 10^{-6} g.

Note that, as mentioned before, the filtration is preferably performed by removing rough impurities by using the filter aid in the first filtration, then removing fine insolubles in the second filtration in the operation. For stabilizing the quality, the purified transparent or semi-transparent filtrate is neutralized by an alkali metal hydroxide, for example, caustic soda or caustic potash, or an alkali carbonate metal salt, for example a sodium carbonate and sodium bicarbonate. In this case, from the viewpoint of the stabilization of quality of the pectin, suitably the pH is stopped at about 3 to 6.

Example 2

1.5 liters of water was added to 500 g of the washed squeezed lees of fruit juice of apples the same as that in Example 1 in the same way as Example 1, 10 g (2 wt% with respect to the material) of benzyltrimethyl ammonium chloride (guaranteed reagent

made by Nakarai Chemicals Ltd.) was added, and thereupon the operation was performed in the same way as that in Example 1 for the decomposition and extraction. The yield of the purified filtrate was 1,510 g. The pectin content in this filtrate was 3,960 γ/ml in terms of galacturonic acid.

Example 3

1.5 liters of water was added to 500 g of the washed squeezed lees of fruit juice of apples the same as that in Example 1 in the same way as Example 1, 85 g (5.1 wt% with respect to the material) of Catiogen L (trademark, made by Daiichi Kogyo Seiyaku Co., Ltd., alkyltrimethyl ammonium chloride, purity 30%) was added, and thereafter the operation was carried out in the same way as that in Example 1 for the decomposition and extraction. The yield of the purified filtrate was 1,700 g, and the pectin content in this filtrate was 3,800 γ/ml in terms of galacturonic acid.

Example 4

1.5 liters of water was added to 500 g of the washed squeezed lees of fruit juice of apples the same as that in Example 1 in the same way as Example 1, 100 g (5 wt% with respect to the material) of Catiogen H (trademark, made by Daiichi Kogyo Seiyaku Co., Ltd.), alkylpicolinium chloride, purity 25%) and 10 g (2 wt% with respect to the material) of a tetrapolyphosphate sodium salt were added, and thereafter the operation was carried out below in the same way as that in Example 1 for the decomposition and extraction. The yield of the purified filtrate was 1,650 g, but considerable coloring was confirmed. The pectin content in this filtrate was 4,500 γ/ml in terms of galacturonic acid.

Comparative Example 1

1.5 liters of water was added to 500 g of the washed squeezed lees of fruit juice of apples the same as that in Example 1 and the result heated. When the liquid temperature became 80°C, dilute sulfuric acid was added to adjust the pH to 3, then the result was heated and stirred at the same temperature for 1 hour for decomposition and extraction in the same way as Examples 1 to 4, but no quaternary ammonium salt or base thereof or inorganic salt was added. Thereafter, the same operation was carried out. The yield of the purified filtrate was 1,230 g, and the pectin content in this filtrate was 2,750 γ/ml in terms of galacturonic acid. Unlike Examples 1 to 4, the extraction residue was viscous, so the filtration was difficult.

Comparative Example 2

10 g (2 wt% with respect to the material) of a tetrapolyphosphate sodium salt was added to 500 g of the washed squeezed lees of fruit juice of apples the same as that in Example 1, the temperature was elevated to 80°C, and the pH was adjusted to 3 by

dilute sulfuric acid. Thereafter, the operation was carried out in the same way as Examples 1 to 4 and Comparative Example 1 to thereby obtain 1,256 g of purified filtrate. The content of the pectin in this filtrate was 2,700 γ/ml in terms of galacturonic acid. In the same way as Comparative Example 1, the extraction residue was viscous, so the filtration was difficult.

Example 5

1.2 liters of water was added to 300 g of the washed squeezed lees of lemons, 0.3 g (0.1 wt% with respect to the material) of benzyltrimethyl ammonium chloride was added, and the result was heated. When the liquid temperature became 80°C, dilute sulfuric acid was added to adjust the pH to 2, then the mixture was heated and stirred at the same temperature for 1 hour for decomposition and extraction. Next, filtration, purification, filtration, and neutralization were carried out. The yield after this purification and filtration was 1,460 g, and the content of the pectin contained in that was 2,400 γ/ml in terms of galacturonic acid.

Comparative Example 3

1.2 liters of water was added to 300 g of the washed squeezed lees of lemons the same as that of Example 5 and the result heated and stirred with no inorganic salt or quaternary ammonium salt or base thereof added. When the liquid temperature became 80°C, the diluted sulfuric acid was added to adjust the pH to 2. Thereafter, the operation was carried out in the same way as Examples 1 to 5 and Comparative Examples 1 and 2. The yield of the thus obtained purified filtrate was 1,260 g, and the content of the pectin contained in that was 2,270 γ/ml in terms of galacturonic acid.

Example 6

The purified filtrate obtained in Example 2 mentioned above was condensed under reduced pressure of 50 mm/Hg at 60°C by using a rotary evaporator, the obtained condensed liquid was centrifuged, and the thus generated floating substance was removed to purify the remainder. 200 ml of isopropyl alcohol was dropped into 100 g of this purified liquid with stirring to precipitate the pectin, the precipitate was extracted by filtration, the precipitate was washed by 60% isopropyl alcohol and further washed by 87% isopropyl alcohol and then ethylether, then dried under reduced pressure at room temperature until obtaining a constant amount, whereupon 0.998 g of almost white pectin was obtained. Using a mixed aqueous solution of a 0.4% aqueous solution of sodium hexametaphosphate and a 0.6% aqueous solution of sodium chloride and adjusted in pH to 6, solutions of 0.2%, 0%, 15%, 0.1%, and 0.05% (g/ml) of this pectin were prepared. The viscosities were measured at 30°± 0.05°C. As a viscometer, an Ostwald viscometer was used. As a result, the limit viscosity thereof was found as 3.47,

and the pectin grade was about 155 based on a report by Messrs. Miura and Mizuta carried in *Reports of Food Laboratory*, vol. 14, pp. 6 to 8 (1959). Further, the molecular weight thereof was estimated as about 74,000 according to P. E. Christensen, *Food Res.* 19, 163 to 172 (1954). Further, the result was confirmed as being pectin by taking its infrared absorption spectrum. At the same time, no existence of even a fine amount of the quaternary ammonium salt was confirmed.

As described above, in order to obtain a pectin as a final product, the purified filtrate is first condensed under reduced pressure. This is done in order to reduce the amount of alcohol required for the precipitation and settling of the pectin by alcohol to be performed next by reducing the amount of the purified filtrate by condensation and, at the same time, improve the action and effect as a precipitation agent. Usually, use is made of 1 part or 2 parts of 60 to 70 vol% alcohol as the settling precipitation agent (nonsolvent) with respect to 1 part of the condensed purified filtrate in order to cause the pectin to precipitate and settle from the purified filtrate. If washing the obtained precipitate of the pectin again by 60 to 70 vol% alcohol and further washing it by a high purity (about 90 vol% or more) alcohol for purification, then drying at 90°C or less under reduced pressure, a high purity product is obtained. Further, as the alcohol to be used, suitable use is made of an aliphatic primary alcohol having 1 to 5 carbon atoms, preferably methyl alcohol, ethyl alcohol, propyl alcohol, or isopropyl alcohol as an aliphatic primary alcohol having 1 to 3 carbon atoms.

Example 7

The purified filtrate obtained in Example 5 was condensed, then centrifuged in the same way as Example 6, then the pectin was precipitated by isopropyl alcohol, washed, purified, and dried, whereby 1.848 g of white pectin was obtained. The viscosity was measured in the same way as Example 6. As a result, the limit viscosity thereof was 2.75, the pectin grade was about 110, and the molecular weight thereof was estimated to be about 59,000. Further, the infrared absorption spectrum of this pectin was taken, whereby the substance was confirmed as pectin and, at the same time, no residue of the quaternary ammonium salt was confirmed.

Example 8

850 ml of water was added to 50 g of dried squeezed lees of sugar beet (beet, sugar beet), 105 g (0.21 wt% with respect to the material) of benzyltrimethyl ammonium chloride was added to this, then the result was heated and stirred. In the same way as Example 1, the pH was adjusted to 3, then the result was decomposed and extracted, then filtered, then centrifugally separated and adjusted in pH to 6, whereby 550 g of the purified filtrate was obtained. The pectin content in this solution was 3,860

γ/ml in terms of galacturonic acid.

Example 9

850 ml of water was added to 50 g of dried squeezed lees of sugar beet the same as that in Example 8, 0.24 g (0.48 wt% with respect to the material) of benzyltrimethyl ammonium chloride was added to this, then the result was heated and stirred. When the liquid temperature became 80°C, 2 g (4 wt% with respect to the material) of sodium hexametaphosphate and dilute sulfuric acid were added to adjust the pH to 2, then the operation was carried out in the same way as Example 1 to obtain 560 g of the purified filtrate. The content of the pectin in this solution was 6,080 γ/ml in terms of galacturonic acid.

Example 10

850 ml of water was added to 50 g of dried squeezed lees of sugar beet the same as that in Example 8, 3.3 g (1.88 wt% with respect to the material) of Catiogen L was added to this, then the result was heated and stirred. When the liquid temperature became 80°C, 2 g (4 wt% with respect to the material) of table salt and dilute sulfuric acid were added to adjust the pH to 2, then the operation was carried out in the same way as Example 1 to obtain 540 g of the purified filtrate. The content of the pectin in this solution was 6,100 γ/ml in terms of galacturonic acid.

Comparative Example 4

850 ml of water was added to 50 g of dried squeezed lees of sugar beet the same as that in Example 8, then the result was heated and stirred. When the liquid temperature became 80°C, dilute sulfuric acid was added to adjust the pH to 3, then the result was heated and stirred at the same temperature for 1 hour for decomposition and extraction in exactly the same way as Examples 8 to 10, but no quaternary ammonium salt or inorganic salt was added. The yield of the obtained purified filtrate was 500 g, and the content of the pectin in this solution was 3,240 γ/ml in terms of galacturonic acid. The filtration was difficult in comparison with Examples 8 and 9.

Example 11

300 ml of water was added to 100 g of squeezed lees of fruit juice of mandarin oranges made in Arita, 11 g (4.4 wt% with respect to the material) of alkylbenzyl dimethyl ammonium chloride (made by Meisei Chemical Work, Ltd., purity 40%) was added to this, and the result was heated and stirred. Thereafter, the same procedure was followed as in Example 1 to obtain 400 g of the purified filtrate. The content of the pectin in this solution was 8.120 γ/ml in terms of galacturonic acid, and the total amount of the pectin in the filtrate was about 3.2 g. Note that 100 g of this purified filtrate was centrifuged to remove the floating substances again, then the same procedure was

followed as in Example 6 to obtain 0.508 g of a yellowish white pectin.This was measured for viscosity in the same way as Example 6, whereupon the limit viscosity (30°C) was found to be 4.16, the pectin grade was about 190, and the molecular weight thereof was estimated to be about 88,000.

Comparative Example 5

300 ml of water was added to 100 g of the squeezed lees of fruit juice of mandarin oranges made in Arita the same as that in Example 11, then the result was heated and stirred without adding the quaternary ammonium salt or the base thereof or an inorganic salt. Thereafter, the same procedure was followed as in Example 11 to obtain 320 g of purified filtrate. The content of the pectin in the filtrate was 9,100 γ/ml, and the total amount of the pectin in the filtrate was about 2.9 g.